

Flowable PVC

Description

- 5 The invention relates to thermoplastic molding compositions comprising
- A) from 10 to 99.99% by weight of at least one polyvinyl chloride (PVC),
 - B) from 0.01 to 50% by weight of
 - 10 B1) at least one highly branched or hyperbranched polycarbonate
or
 - B2) at least one highly branched or hyperbranched polyester of the A_xB_y type
where x is at least 1.1 and y is at least 2.1
or mixtures thereof
 - 15 C) from 0 to 60% by weight of further additives,
- the sum of the percentages by weight of components A) to C) adding up to 100%.

The invention further relates to the use of the inventive molding compositions for producing fibers, films and moldings, and also to the moldings of any type obtainable in this way.

To improve the flowability, low molecular weight additives are typically added to thermoplastics. However, the action of such additives is highly restricted, since, for example, the decline in the mechanical properties is no longer tolerable when the amount of the additive added is increased, and the effectiveness of the flame retardancy usually also decreases.

Dendritic polymers having a perfectly symmetrical structure, known as dendrimers, can be prepared starting from one central molecule via controlled stepwise linkage of in each case two or more di- or polyfunctional monomers to each previously bonded monomer. Each linkage step exponentially increases the number of monomer end groups (and therefore of linkages), and this gives polymers with treelike structures, in the ideal case spherical, the branches of which comprise exactly the same number of monomer units. Owing to this perfect structure, the polymer properties are advantageous: for example, surprisingly low viscosity is found, as is high reactivity owing to the large number of functional groups on the surface of the sphere. However, the preparation is complicated by the fact that protecting groups have to be introduced and removed again in each linkage step, and purification operations are required, which is why dendrimers are typically prepared only on the laboratory scale.

40 However, highly branched or hyperbranched polymers can be prepared using industrial scale processes. In addition to perfect dendritic structures, they also have linear polymer chains and unequal polymer branches, which does not, however, substantially

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impair the polymer properties in comparison to those of the perfect dendrimers. Hyperbranched polymers can be prepared via two synthetic routes known as AB_2 and $A_x + B_y$. Here, A_x and B_y are different monomers and the indices x and y are the number of functional groups present in A and B respectively, i.e. the functionality of A and B respectively. In the AB_2 route, a trifunctional monomer having a reactive group A and having two reactive groups B is converted to a highly branched or hyperbranched polymer. In the $A_x + B_y$ synthesis, illustrated using the example of the $A_2 + B_3$ synthesis, a difunctional monomer A_2 is reacted with a trifunctional monomer B_3 . This first gives a 1:1 adduct of A and B having an average of one functional group A and two functional groups B, which can then likewise react to give a highly branched or hyperbranched polymer.

WO-97/45474 discloses thermoplastic compositions which comprise dendrimeric polyesters as the AB_2 molecule. In this case, a polyhydric alcohol as core molecule reacts with dimethylolpropionic acid as the AB_2 molecule to give a dendrimeric polyester. This comprises only OH functions at the end of the chain. Disadvantages of these mixtures are high glass transition temperature of the dendrimeric polyesters, the comparatively complicated preparation, and in particular poor solubility of the dendrimers in the polyester matrix.

According to the teaching of DE-A 101 32 928, the incorporation of branching agents of this type by means of compounding and solid-phase postcondensation leads to an improvement in mechanical properties (molecular weight increase). The disadvantages of the process variant described are long preparation time and the disadvantageous properties listed above.

DE 102004 005652.8 and DE 102004 005657.9 have previously proposed novel additives for flow improvement in polyesters.

It was therefore an object of the present invention to provide thermoplastic polyvinyl chloride molding compositions which have good flowability and simultaneously good mechanical properties. In particular, the additive should not have any tendency to exudation or to mold deposition.

As component (A), the inventive molding compositions comprise from 10 to 99.99% by weight, preferably from 30 to 98% by weight and in particular from 30 to 95% by weight, of at least one polyvinyl chloride.

Depending on the content of plasticizers, a distinction is drawn between hard PVC (< 0.1% plasticizers) and soft PVC (> 0.1% plasticizers).

Polyvinyl chloride is obtained typically by homopolymerization of vinyl chloride. The

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polyvinyl chloride (PVC) used in accordance with the invention may be prepared, for example, by suspension polymerization, microsuspension polymerization, emulsion polymerization or bulk polymerization. The preparation of PVC by polymerization of vinyl chloride, and preparation and composition of plasticized PVC, are described, for example, in "Becker/Braun, Kunststoff-Handbuch" [Plastics Handbook], Volume 2/1: "Polyvinyl chloride", 2nd edition, Carl Hanser Verlag, Munich.

The K value which characterizes the molar mass of the PVC and is determined to DIN 53726 is, for the inventive PVC, from 57 to 90, preferably from 61 to 85, in particular from 64 to 75.

As component B), the inventive molding compositions comprise from 0.01 to 50% by weight, preferably from 0.5 to 20% by weight and in particular from 0.7 to 10% by weight, of B1) at least one highly branched or hyperbranched polycarbonate, preferably having an OH number of from 1 to 600 mg KOH/g of polycarbonate, preferably from 10 to 550 mg KOH/g of polycarbonate and in particular from 50 to 550 mg KOH/g of polycarbonate (to DIN 53240, part 2), or of at least one hyperbranched polyester as component B2) or mixtures thereof as described below.

In the context of this invention, hyperbranched polycarbonates B1) are uncrosslinked macromolecules having hydroxyl groups and carboxyl groups which have both structural and molecular non-uniformity. One possible structure is based on a central molecule in the same way as dendrimers, but with non-uniform chain length of the branches. Another possibility is a linear structure with functional pendant groups, or else a combination of the two extremes, with linear and branched molecular portions. See also P.J. Flory, J. Am. Chem. Soc. 1952, 74, 2718, and H. Frey et al., Chem. Eur. J. 2000, 6, No. 14, 2499 for the definition of dendrimeric and hyperbranched polymers.

"Hyperbranched" in the context of the present invention means that the degree of branching (DB), i.e. the average number of dendritic linkages plus the average number of end groups per molecule, is from 10 to 99.9%, preferably from 20 to 99%, more preferably from 20 to 95%.

"Dendrimeric" in the context of the present invention means that the degree of branching is from 99.9 to 100%. See H. Frey et al., Acta Polym. 1997, 48, 30 for the definition of "degree of branching" and is defined as

$$DB = \frac{T+Z}{T+Z+L} \times 100\%,$$

(where T is the average number of terminal monomer units, Z the average number of

branched monomer units and L the average number of linear monomer units in the macromolecules of the particular substances).

- Component B1) preferably has a number-average molecular weight M_n of from 100 to 15 000 g/mol, preferably from 200 to 12 000 g/mol and in particular from 500 to 10 000 g/mol (GPC, PMMA standard).

- The glass transition temperature T_g is in particular from -80°C to $+140^\circ\text{C}$, preferably from -60 to 120°C (by DSC, DIN 53765).

- In particular, the viscosity (mPas) at 23°C (to DIN 53019) is from 50 to 200 000, in particular from 100 to 150 000 and most preferably from 200 to 100 000.

- Component B1) is preferably obtainable by a process which comprises at least the following steps:

- a) reaction of at least one organic carbonate (A) of the general formula $\text{RO}[(\text{CO})_n\text{OR}]$ with at least one aliphatic, araliphatic or aromatic alcohol (B) which has at least 3 OH groups with elimination of alcohols ROH to give one or more condensation products (K), where R is in each case independently a straight-chain or branched, aliphatic, araliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms, and where the R radicals may also be joined together to form a ring and n is an integer from 1 to 5, or
- ab) reaction of phosgene, diphosgene or triphosgene with the abovementioned alcohol (B) with hydrogen chloride elimination

and

- b) intermolecular reaction of the condensation products (K) to give a highly functional highly branched or highly functional hyperbranched polycarbonate,

- the quantitative ratio of the OH groups to the carbonates in the reaction mixture being selected in such a way that the condensation products (K) have an average either of one carbonate group and more than one OH group or one OH group and more than one carbonate group.

- The starting material used may be phosgene, diphosgene or triphosgene, and preference is given to organic carbonates.

- Each of the R radicals of the organic carbonates (A) used as a starting material and having the general formula $\text{RO}[(\text{CO})_n\text{OR}]$ is independently a straight-chain or branched

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- aliphatic, araliphatic, or aromatic hydrocarbon radical having from 1 to 20 carbon atoms. The two R radicals may also be joined together to form a ring. The radical is preferably an aliphatic hydrocarbon radical and more preferably a straight-chain or branched alkyl radical having from 1 to 5 carbon atoms, or a substituted or unsubstituted phenyl radical.

In particular, simple carbonates of the formula $RO(CO)_nOR$ are used; n is preferably from 1 to 3, in particular 1.

- 10 Dialkyl or diaryl carbonates may be prepared, for example, from the reaction of aliphatic, araliphatic or aromatic alcohols, preferably monoalcohols, with phosgene. They may also be prepared via oxidative carbonylation of the alcohols or phenols by means of CO in the presence of noble metals, oxygen, or NO_x . In relation to preparation methods for diaryl or dialkyl carbonates, see also "Ullmann's Encyclopedia of Industrial Chemistry", 6th edition, 2000 Electronic Release, Verlag Wiley-VCH.

- Examples of suitable carbonates comprise aliphatic, araliphatic or aromatic carbonates, such as ethylene carbonate, propylene 1,2- or 1,3-carbonate, diphenyl carbonate, ditolyl carbonate, dixyl carbonate, dinaphthyl carbonate, ethyl phenyl carbonate, dibenzyl carbonate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate, diisobutyl carbonate, dipentyl carbonate, dihexyl carbonate, dicyclohexyl carbonate, diheptyl carbonate, dioctyl carbonate, didecyl carbonate, or didodecyl carbonate.

- 25 Examples of carbonates in which n is greater than 1 comprise dialkyl dicarbonates such as di(t-butyl) dicarbonate, or dialkyl tricarbonates such as di(t-butyl) tricarbonate.

- Preference is given to using aliphatic carbonates, in particular those in which the radicals comprise from 1 to 5 carbon atoms, for example dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate or diisobutyl carbonate.

The organic carbonates are reacted with at least one aliphatic alcohol (B) which has at least 3 OH groups, or mixtures of two or more different alcohols.

- 35 Examples of compounds having at least three OH groups comprise glycerol, trimethylolmethane, trimethylolethane, trimethylolpropane, 1,2,4-butanetriol, tris(hydroxymethyl)-amine, tris(hydroxyethyl)amine, tris(hydroxypropyl)amine, pentaerythritol, diglycerol, triglycerol, polyglycerols, bis(trimethylolpropane), tris(hydroxymethyl) isocyanurate, tris(hydroxyethyl) isocyanurate, phloroglucinol, trihydroxytoluene, trihydroxydimethylbenzene, phloroglucides, hexahydrobenzene, 1,3,5-benzenetrimethanol, 1,1,1-tris(4'-hydroxyphenyl)methane, 1,1,1-tris(4'-hydroxyphenyl)ethane, bis(trimethylolpropane), or sugars, for example glucose, trihy-

dric or higher polyhydric polyetherols based on trihydric or higher polyhydric alcohols and ethylene oxide, propylene oxide, or butylene oxide, or polyesterols. Particular preference is given to glycerol, trimethylethane, trimethylpropane, 1,2,4-butanetriol, pentaerythritol, and also their polyetherols based on ethylene oxide or propylene oxide.

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These polyhydric alcohols may also be used in a mixture with dihydric alcohols (B'), with the proviso that the average total OH functionality of all of the alcohols used is greater than 2. Examples of suitable compounds having two OH groups comprise ethylene glycol, diethylene glycol, triethylene glycol, 1,2- and 1,3-propanediol, dipropylene glycol, tripropylene glycol, neopentyl glycol, 1,2-, 1,3-, and 1,4-butanediol, 1,2-, 1,3-, and 1,5-pentanediol, hexanediol, cyclopentanediol, cyclohexanediol, cyclohexanedi-methanol, bis(4-hydroxycyclohexyl)methane, bis(4-hydroxycyclohexyl)-ethane, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1'-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, resorcinol, hydroquinone, 4,4'-dihydroxyphenyl, bis(4-bis-(hydroxyphenyl) sulfide, bis(4-hydroxyphenyl) sulfone, bis(hydroxymethyl)benzene, bis(hydroxymethyl)toluene, bis(p-hydroxyphenyl)methane, bis(p-hydroxyphenyl)-ethane, 2,2-bis(p-hydroxyphenyl)propane, 1,1-bis(p-hydroxyphenyl)cyclohexane, dihydroxybenzophenone, dihydric polyether polyols based on ethylene oxide, propylene oxide, butylene oxide, or a mixture of these, polytetrahydrofuran, polycaprolactone, or polyesterols based on diols and dicarboxylic acids.

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The diols serve for fine adjustment of the properties of the polycarbonate. If dihydric alcohols are used, the ratio of dihydric alcohols (B') to the at least trihydric alcohols (B) is set by the person skilled in the art as a function of the desired properties of the polycarbonate. The amount of the alcohol(s) (B') is generally from 0 to 50 mol%, based on the total amount of all alcohols (B) and (B'). The amount is preferably from 0 to 45 mol%, more preferably from 0 to 35 mol%, and most preferably from 0 to 30 mol%.

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The reaction of phosgene, diphosgene, or triphosgene with the alcohol or alcohol mixture generally takes place with elimination of hydrogen chloride, and the reaction of the carbonates with the alcohol or alcohol mixture to give the inventive highly functional highly branched polycarbonate takes place with elimination of the monohydric alcohol or phenol from the carbonate molecule.

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After the reaction, i.e. with no further modification, the highly functional highly branched polycarbonates formed by the inventive process are terminated by hydroxyl groups and/or by carbonate groups. They have good solubility in various solvents, for example in water, alcohols, such as methanol, ethanol, butanol, alcohol/water mixtures, acetone, 2-butanone, ethyl acetate, butyl acetate, methoxypropyl acetate, methoxyethyl acetate, tetrahydrofuran, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, ethylene carbonate or propylene carbonate.

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In the context of this invention, a highly functional polycarbonate is a product which, in addition to the carbonate groups which form the polymer skeleton, further has at least three, preferably at least six, more preferably at least ten, terminal or pendant functional groups. The functional groups are carbonate groups and/or OH groups. There is

- 5 in principle no upper restriction on the number of the terminal or pendant functional groups, but products having a very high number of functional groups can have undesired properties, such as high viscosity or poor solubility. The highly functional polycarbonates of the present invention usually have not more than 500 terminal or pendant functional groups, preferably not more than 100 terminal or pendant functional groups.

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In the preparation of the highly functional polycarbonates B1), it is necessary to adjust the ratio of the compounds comprising OH groups to phosgene or carbonate in such a way that the simplest resulting condensation product (hereinafter termed condensation product (K)) comprises an average of either one carbonate group or carbamoyl group and more than one OH group or one OH group and more than one carbonate group or carbamoyl group. The simplest structure of the condensation product (K) composed of a carbonate (A) and a di- or polyalcohol (B) gives rise to the XY_n or Y_nX arrangement where X is a carbonate group, Y is a hydroxyl group, and n is generally a number from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3. The reactive group which is

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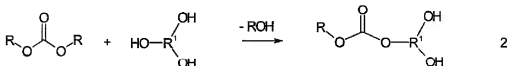
For example, when the reaction ratio in the preparation of the simplest condensation product (K) from a carbonate and a dihydric alcohol is 1:1, the average result is a molecule of XY type, illustrated by the general formula 1.

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In the preparation of the condensation product (K) from a carbonate and a trihydric alcohol with a reaction ratio of 1:1, the average result is a molecule of XY_2 type, illustrated by the general formula 2. The focal group here is a carbonate group.

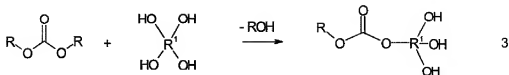
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In the preparation of the condensation product (K) from a carbonate and a tetrahydric alcohol, likewise with the reaction ratio 1:1, the average result is a molecule of XY_3 type, illustrated by the general formula 3. The focal group here is a carbonate group.

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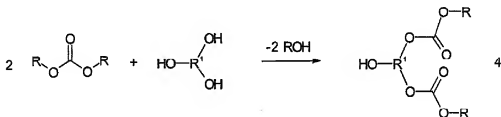


In the formulae 1-3, R is as defined at the outset and R' is an aliphatic or aromatic radical.

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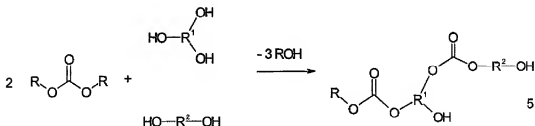
The condensation product (K) can also be prepared, for example, from a carbonate and a trihydric alcohol, illustrated by the general formula 4, the molar reaction ratio being 2:1. Here, the average result is a molecule of X₂Y type; the focal group here is an OH group. In the formula 4, R and R' are each as defined in the formulae 1-3.

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When difunctional compounds, for example a dicarbonate or a diol, are additionally added to the components, this brings about an extension of the chains, as illustrated in the general formula 5, for example. The average result is again a molecule of XY₂ type; the focal group is a carbonate group.

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20 In formula 5, R² is an organic, preferably aliphatic radical; R and R' are each as defined above.

It is also possible to use two or more condensation products (K) for the synthesis. It is possible in this context firstly to use a plurality of alcohols or a plurality of carbonates. It is also possible to obtain mixtures of various condensation products of different structure by virtue of the selection of the ratio of the alcohols used and of the carbonates or of the phosgenes. This will be explained using the example of the reaction of a carbonate with a trihydric alcohol. If the starting materials are introduced in a ratio of 1:1, as

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illustrated in (II), the result is an XY_2 molecule. When the starting materials are used in a ratio of 2:1, as illustrated in (IV), an X_2Y molecule is obtained. At a ratio between 1:1 and 2:1, a mixture of XY_2 and X_2Y molecules is obtained.

- 5 According to the invention, the simple condensation products (K) described by way of example in the formulae 1-5 preferentially react intermolecularly to form highly functional polycondensation products, hereinafter referred to as polycondensation products (P). The reaction to give the condensation product (K) and to give the polycondensation product (P) usually takes place at a temperature of from 0 to 250°C, preferably
- 10 from 60 to 160°C, in bulk or in solution. It is generally possible to use all solvents which are inert toward the particular reactants. Preference is given to using organic solvents, for example decane, dodecane, benzene, toluene, chlorobenzene, xylene, dimethylformamide, dimethylacetamide or Solvent Naphtha.
- 15 In a preferred embodiment, the condensation reaction is carried out in bulk. The phenol or the monohydric alcohol ROH released in the reaction can be removed by distillation from the reaction equilibrium to accelerate the reaction, if appropriate under reduced pressure.
- 20 If removal by distillation is intended, it is regularly advisable to use those carbonates which liberate alcohols ROH having a boiling point below 140°C in the reaction.

To accelerate the reaction, it is also possible to add catalysts or catalyst mixtures. Suitable catalysts are compounds which catalyze esterification or transesterification reactions,

25 for example alkali metal hydroxides, alkali metal carbonates, alkali metal hydrogencarbonates, preferably of sodium, of potassium or of cesium, tertiary amines, guanidines, ammonium compounds, phosphonium compounds, organoaluminum, organotin, organozinc, organotitanium, organozirconium or organobismuth compounds, or else what are known as double metal cyanide (DMC) catalysts, as described, for example,

30 in DE 10138216 or DE 10147712.

- Preference is given to using potassium hydroxide, potassium carbonate, potassium hydrogencarbonate, diazabicyclooctane (DABCO), diazabicyclononene (DBN), diazabicycloundecene (DBU), imidazoles such as imidazole, 1-methylimidazole or
- 35 1,2-dimethylimidazole, titanium tetrabutoxide, titanium tetraisopropoxide, dibutyltin oxide, dibutyltin dilaurate, tin dioctoate, zirconium acetylacetonate or mixtures thereof.

- The catalyst is generally added in an amount of from 50 to 10 000 ppm by weight, preferably from 100 to 5000 ppm by weight, based on the amount of the alcohol mixture or
- 40 alcohol used.

It is also possible to control the intermolecular polycondensation reaction by addition of

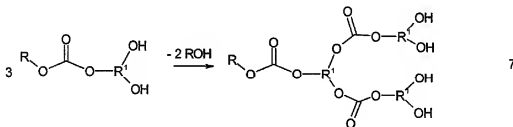
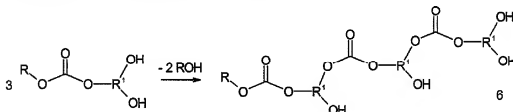
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the suitable catalyst or else by selection of a suitable temperature. It is also possible to adjust the average molecular weight of the polymer (P) via the composition of the starting components and via the residence time.

- 5 The condensation products (K) and the polycondensation products (P) prepared at elevated temperature are typically stable at room temperature for a prolonged period.

- The nature of the condensation products (K) makes it possible for the condensation reaction to result in polycondensation products (P) with different structures, which have
10 branching but no crosslinking. Moreover, in the ideal case, the polycondensation products (P) have either one carbonate group as focal group and more than two OH groups or else one OH group as focal group and more than two carbonate groups. The number of the reactive groups depends on the nature of the condensation products (K) used and the degree of polycondensation.

- 15 For example, a condensation product (K) of the general formula 2 can react by triple intermolecular condensation to give two different polycondensation products (P) which are represented in the general formulae 6 and 7:



In formulae 6 and 7, R and R¹ are each as defined above.

- 25 For the termination of the intermolecular polycondensation reaction, there are various methods. For example, the temperature can be lowered to a range in which the reaction stops and the product (K) or the polycondensation product (P) is storage-stable.

- 30 It is also possible to deactivate the catalyst, for example by addition of Lewis acids or protic acids in the case of basic catalysts.

In another embodiment, as soon as a polycondensation product (P) with the desired

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- degree of polycondensation is present as a result of the intermolecular reaction of the condensation product (K), a product having groups reactive toward the focal group of (P) may be added to the product (P) to terminate the reaction. For example, in the case of a carbonate group as focal group, a mono-, di-, or polyamine may be added. In the case of a hydroxyl group as focal group, for example, a mono-, di- or polyisocyanate, a compound comprising epoxy groups or an acid derivative which reacts with OH groups can be added to the product (P).

- The inventive highly functional polycarbonates are usually prepared in a pressure range from 0.1 mbar to 20 bar, preferably at from 1 mbar to 5 bar, in reactors or reactor batteries which are operated batchwise, semicontinuously or continuously.

- By virtue of the abovementioned adjustment of the reaction conditions and, if appropriate, by virtue of the selection of the suitable solvent, the inventive products can be further processed without further purification after their preparation.

- In a further preferred embodiment, the product is stripped, i.e. freed of low molecular weight, volatile compounds. To this end, once the desired degree of conversion has been attained, the catalyst may optionally be deactivated and the low molecular weight, volatile constituents, for example monoalcohols, phenols, carbonates, hydrogen chloride or highly volatile oligomeric or cyclic compounds, can be removed by distillation, if appropriate with introduction of a gas, preferably nitrogen, carbon dioxide or air, if appropriate at reduced pressure.

- In a further preferred embodiment, the inventive polycarbonates may obtain other functional groups in addition to the functional groups already present as a result of the reaction. The functionalization may take place during the molecular weight buildup, or else subsequently, i.e. after completion of the actual polycondensation.

- When, prior to or during the molecular weight buildup, components are added which have further functional groups or functional elements in addition to hydroxyl or carbonate groups, a polycarbonate polymer with randomly distributed functionalities other than the carbonate or hydroxyl groups is obtained.

- These effects can, for example, be achieved by addition, during the polycondensation, of compounds which bear further functional groups or functional elements, such as mercapto groups, primary, secondary or tertiary amino groups, ether groups, derivatives of carboxylic acids, derivatives of sulfonic acids, derivatives of phosphonic acids, silane groups, siloxane groups, aryl radicals or long-chain alkyl radicals, in addition to hydroxyl groups, carbonate groups or carbamoyl groups. For modification by means of carbamate groups, it is possible, for example, to use ethanolamine, propanolamine, isopropanolamine, 2-(butylamino)ethanol, 2-(cyclohexylamino)ethanol, 2-amino-1-

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- butanol, 2-(2'-aminoethoxy)ethanol or higher alkoxylation products of ammonia, 4-hydroxypiperidine, 1-hydroxyethylpiperazine, diethanolamine, dipropanolamine, diisopropanolamine, tris(hydroxymethyl)aminomethane, tris(hydroxyethyl)amino-]methane, ethylenediamine, propylenediamine, hexamethylenediamine or isophoronediamine.

- For modification with mercapto groups, it is possible, for example, to use mercaptoethanol. By way of example, tertiary amino groups can be produced via incorporation of N-methyldiethanolamine, N-methyldipropanolamine or N,N-dimethylethanolamine.
- 10 Ether groups can be obtained, for example, by cocondensation of dihydric or higher polyhydric polyetherols. Reaction with long-chain alkanediols can introduce via reaction long-chain alkyl radicals; reaction with alkyl or aryl diisocyanates generates polycarbonates having alkyl, aryl, and urethane groups or urea groups.
- 15 Addition of dicarboxylic acids or tricarboxylic acids, for example dimethyl terephthalate or tricarboxylic esters, allows ester groups to be obtained.

- Subsequent functionalization can be obtained by reacting the resulting highly functional highly branched or highly functional hyperbranched polycarbonate in an additional
- 20 process step (step c)) with a suitable functionalizing reagent which can react with the OH and/or carbonate groups or carbamoyl groups of the polycarbonate.

- Highly functional highly branched or highly functional hyperbranched polycarbonates comprising hydroxyl groups can be modified, for example, by addition of molecules
- 25 comprising acid groups or isocyanate groups. For example, polycarbonates comprising acid groups can be obtained by reaction with compounds comprising anhydride groups.

- Moreover, highly functional polycarbonates comprising hydroxyl groups can also be converted to highly functional polycarbonate polyether polyols by reaction with alkylene
- 30 oxides, for example ethylene oxide, propylene oxide, or butylene oxide.

- A great advantage of the process lies in its economic viability. Both the reaction to give a condensation product (K) or polycondensation product (P) and the reaction of (K) or (P) to give polycarbonates with other functional groups or elements can take place in
- 35 one reaction apparatus, which is technically and economically advantageous.

As component B2), the inventive molding compositions may comprise at least one hyperbranched polyester of A₂B₃ type where

- 40 x is at least 1.1, preferably at least 1.3, in particular at least 2
y is at least 2.1, preferably at least 2.5, in particular at least 3.

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It is of course also possible to use mixtures as units A and/or B.

- 5 An A_xB_y-type polyester is a condensate composed of an x-functional molecule A and a y-functional molecule B. An example is a polyester composed of adipic acid as molecule A (x = 2) and glycerol as molecule B (y = 3).

- 10 In the context of this invention, hyperbranched polyesters B2) are uncrosslinked macromolecules having hydroxyl groups and carboxyl groups which have both structural and molecular non-uniformity. One possible structure is based on a central molecule in the same way as dendrimers, but with non-uniform chain length of the branches. Another possibility is a linear structure with functional pendant groups, or else a combination of the two extremes, with linear and branched molecular portions. See also P.J. Flory, J. Am. Chem. Soc. 1952, 74, 2718, and H. Frey et al., Chem. Eur. J. 2000, 6, No. 14, 2499 for the definition of dendrimeric and hyperbranched polymers.

- 15 "Hyperbranched" in the context of the present invention means that the degree of branching (DB), i.e. the average number of dendritic linkages plus the average number of end groups per molecule, is from 10 to 99.9%, preferably from 20 to 99%, more preferably from 20 to 95%.
- 20 "Dendrimeric" in the context of the present invention means that the degree of branching is from 99.9 to 100%. See H. Frey et al., Acta Polym. 1997, 48, 30 and the above formula for B1) for the definition of "degree of branching".

- 25 Component B2) preferably has an M_n of from 300 to 30 000 g/mol, in particular from 400 to 25 000 g/mol and very particularly from 500 to 20 000 g/mol, determined by means of GPC, PMMA standard, dimethylacetamide eluent.

- 30 B2) preferably has an OH number of from 0 to 600 mg KOH/g of polyester, preferably of from 1 to 500 mg KOH/g of polyester, in particular from 20 to 500 mg KOH/g of polyester, to DIN 53240, and preferably a COOH number of from 0 to 600 mg KOH/g of polyester, preferably from 1 to 500 mg KOH/g of polyester, and in particular from 2 to 500 mg KOH/g of polyester.

- 35 The T_g is preferably from -50°C to 140°C, and in particular from -50 to 100°C (by means of DSC, to DIN 53765).

- Preference is given in particular to those components B2) in which at least one OH or COOH number is greater than 0, preferably greater than 0.1 and in particular greater than 0.5.

- 40 The inventive component B2) is in particular obtainable via the processes described below, specifically by reacting

- (a) one or more dicarboxylic acids or one or more derivatives thereof with one or more at least trihydric alcohols,
- 5 or
- (b) one or more tricarboxylic acids or higher polycarboxylic acids or one or more derivatives thereof with one or more diols
- 10 in the presence of a solvent and optionally in the presence of an inorganic, organometallic or low molecular weight organic catalyst, or of an enzyme. The reaction in solvent is the preferred preparation method.
- In the context of the present invention, highly functional hyperbranched polyesters B2)
- 15 have molecular and structural non-uniformity. Their molecular non-uniformity distinguishes them from dendrimers, and they can therefore be prepared at considerably lower cost.
- The dicarboxylic acids which can be reacted according to variant (a) include, for example,
- 20 oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecane- α,ω -dicarboxylic acid, dodecane- α,ω -dicarboxylic acid, cis- and trans-cyclohexane-1,2-dicarboxylic acid, cis- and trans-cyclohexane-1,3-dicarboxylic acid, cis- and trans-cyclohexane-1,4-dicarboxylic acid, cis- and trans-cyclopentane-1,2-dicarboxylic acid, and cis- and trans-cyclopentane-1,3-
- 25 dicarboxylic acid,
- and the abovementioned dicarboxylic acids may be substituted by one or more radicals selected from
- 30 C₁-C₁₀-alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, n-octyl, 2-ethylhexyl, n-nonyl and n-decyl,
- 35 C₃-C₁₂-cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, and cyclododecyl; preference is given to cyclopentyl, cyclohexyl and cycloheptyl;
- alkylene groups such as methylene or ethylene, or
- 40 C₆-C₁₄-aryl groups such as phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl, and 9-phenanthryl,

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preferably phenyl, 1-naphthyl and 2-naphthyl, more preferably phenyl.

Examples of representatives of substituted dicarboxylic acids include: 2-methylmalonic acid, 2-ethylmalonic acid, 2-phenylmalonic acid, 2-methylsuccinic acid, 2-ethylsuccinic acid, 2-phenylsuccinic acid, itaconic acid, 3,3-dimethylglutaric acid.

The dicarboxylic acids which can be reacted according to variant (a) also include ethylenically unsaturated acids, for example maleic acid and fumaric acid, and aromatic dicarboxylic acids such as phthalic acid, isophthalic acid or terephthalic acid.

It is also possible to use mixtures of two or more of the abovementioned representatives.

The dicarboxylic acids may either be used as such or in the form of derivatives.

Derivatives are preferably

- the relevant anhydrides in monomeric or else polymeric form,
- mono- or dialkyl esters, preferably mono- or dimethyl esters, or the corresponding mono- or diethyl esters, or else the mono- and dialkyl esters derived from higher alcohols such as n-propanol, isopropanol, n-butanol, isobutanol, tert-butanol, n-pentanol, n-hexanol,
- and also mono- and divinyl esters, and
- mixed esters, preferably methyl ethyl esters.

In the context of the preferred preparation, it is also possible to use a mixture of a dicarboxylic acid and one or more of its derivatives. Equally, it is possible to use a mixture of a plurality of different derivatives of one or more dicarboxylic acids.

Particularly preference is given to using succinic acid, glutaric acid, adipic acid, phthalic acid, isophthalic acid, terephthalic acid, or their mono- or dimethyl esters. Very particularly preference is given to using adipic acid.

Examples of at least trihydric alcohols which can be reacted are: glycerol, butane-1,2,4-triol, n-pentane-1,2,5-triol, n-pentane-1,3,5-triol, n-hexane-1,2,6-triol, n-hexane-1,2,5-triol, n-hexane-1,3,6-triol, trimethylolbutane, trimethylolpropane or ditrimethylolpropane, trimethylethane, pentaerythritol or dipentaerythritol; sugar alcohols such as mesoerythritol, threitol, sorbitol, mannitol, or mixtures of the above at least trihydric alcohols. Preference is given to using glycerol, trimethylolpropane, trimethylethane

and pentaerythritol.

Examples of tricarboxylic acids or polycarboxylic acids which can be reacted according to variant (b) are benzene-1,2,4-tricarboxylic acid, benzene-1,3,5-tricarboxylic acid,
5 benzene-1,2,4,5-tetracarboxylic acid and mellitic acid.

Tricarboxylic acids or polycarboxylic acids can be used in the inventive reaction either as such or in the form of derivatives.

10 Derivatives are preferably

- the relevant anhydrides in monomeric or else polymeric form,
- mono-, di- or trialkyl esters, preferably mono-, di- or trimethyl esters, or the
15 corresponding mono-, di- or triethyl esters, or else the mono-, di- and triesters derived from higher alcohols such as n-propanol, isopropanol, n-butanol, isobutanol, tert-butanol, n-pentanol, n-hexanol, or else mono-, di- or trivinyl esters
- 20 - and mixed methyl ethyl esters.

In the context of the present invention, it is also possible to use a mixture of a tri- or polycarboxylic acid and one or more of its derivatives. In the context of the present invention it is equally possible to use a mixture of a plurality of different derivatives of one
25 or more tri- or polycarboxylic acids in order to obtain component B2).

Examples of diols used for variant (b) of the present invention are ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,3-diol, butane-1,4-diol, butane-2,3-diol, pentane-1,2-diol, pentane-1,3-diol, pentane-1,4-diol, pentane-1,5-diol,
30 pentane-2,3-diol, pentane-2,4-diol, hexane-1,2-diol, hexane-1,3-diol, hexane-1,4-diol, hexane-1,5-diol, hexane-1,6-diol, hexane-2,5-diol, heptane-1,2-diol, 1,7-heptanediol, 1,8-octanediol, 1,2-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,2-decanediol, 1,12-dodecanediol, 1,2-dodecanediol, 1,5-hexadiene-3,4-diol, cyclopentanediols, cyclohexanediols, inositol and derivatives, 2-methylpentane-2,4-diol, 2,4-dimethyl-
35 pentane-2,4-diol, 2-ethylhexane-1,3-diol, 2,5-dimethylhexane-2,5-diol, 2,2,4-trimethylpentane-1,3-diol, pinacol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, polyethylene glycols $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ or polypropylene glycols $\text{HO}(\text{CH}[\text{CH}_3]\text{CH}_2\text{O})_n\text{H}$ or mixtures of two or more representative compounds of the above compounds, where n is an integer and $n = 4 - 25$. One hydroxyl group or else
40 both hydroxyl groups in the aforementioned diols may also be replaced by SH groups. Preference is given to ethylene glycol, propane-1,2-diol, and diethylene glycol, triethylene glycol, dipropylene glycol, and tripropylene glycol.

The molar ratio of the molecules A to molecules B in the A_nB_m polyester in the variants (a) and (b) is from 4:1 to 1:4, in particular from 2:1 to 1:2.

- 5 The at least trihydric alcohols reacted according to variant (a) of the process may have hydroxyl groups each of the same reactivity. Preference is also given here to at least trihydric alcohols whose OH groups initially have the same reactivity, but where reaction with at least one acid group can induce a decline in reactivity of the remaining OH groups caused by steric or electronic effects. For example, this is the case when
10 trimethylolpropane or pentaerythritol is used.

However, the at least trihydric alcohols reacted according to variant (a) may also have hydroxyl groups having at least two different chemical reactivities.

- 15 The different reactivity of the functional groups may either stem from chemical causes (e.g. primary/secondary/tertiary OH group) or from steric causes.

For example, the triol may be a triol which has primary and secondary hydroxyl groups; the preferred example is glycerol.

- 20 When the inventive reaction is carried out according to variant (a), the triol or the mixture of at least trifunctional alcohols may also be admixed with difunctional alcohols, preferably up to 50 mol% based on the polyol mixture, but preference is given to working in the absence of diols and monohydric alcohols.

- 25 When the inventive reaction is carried out according to variant (b), the tricarboxylic acid or the carboxylic acid mixture of at least trifunctional carboxylic acids may also be admixed with difunctional carboxylic acids, preferably up to 50 mol% based on the acid mixture, but preference is given to working in the absence of mono- or dicarboxylic acids.
30

- The inventive process is carried out in the presence of a solvent. Examples of suitable solvents are hydrocarbons such as paraffins or aromatics. Particularly suitable paraffins are n-heptane and cyclohexane. Particularly suitable aromatics are toluene, ortho-xylene, meta-xylene, para-xylene, xylene in the form of an isomer mixture, ethylbenzene, chlorobenzene and ortho- and meta-dichlorobenzene. Other very particularly
35 suitable solvents in the absence of acidic catalysts are: ethers, for example dioxane or tetrahydrofuran, and ketones, for example methyl ethyl ketone and methyl isobutyl ketone.

- 40 According to the invention, the amount of solvent added is at least 0.1% by weight, based on the mass of the starting materials used and to be reacted, preferably at least

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- 1% by weight and more preferably at least 10% by weight. It is also possible to use excesses of solvent, based on the mass of starting materials used and to be reacted, for example from 1.01 to 10 times the amount. Solvent amounts of more than 100 times the mass of the starting materials used and to be reacted are not advantageous, because the reaction rate declines markedly at markedly lower concentrations of the reactants, which leads to uneconomically long reaction times.

- To carry out the process preferred in accordance with the invention, it is possible to work in the presence of a dehydrating agent as an additive, which is added at the start of the reaction. Suitable examples are molecular sieves, in particular 4 Å molecular sieve, MgSO_4 and Na_2SO_4 . During the reaction, it is also possible to add further dehydrating agent or to replace dehydrating agent with fresh dehydrating agent. During the reaction, it is also possible to distill off the water or alcohol formed and, for example, to use a water separator.

- The process can be carried out in the absence of acidic catalysts. Preference is given to working in the presence of an acidic inorganic, organometallic or organic catalyst, or mixtures of two or more acidic inorganic, organometallic or organic catalysts.

- In the context of the present invention, examples of acidic inorganic catalysts are sulfuric acid, phosphoric acid, hypophosphorous acid, aluminum sulfate hydrate, alum, acidic silica gel (pH = 6, in particular = 5) and acidic aluminum oxide. Further examples of compounds which can be used as acidic inorganic catalysts are aluminum compounds of the general formula $\text{Al}(\text{OR})_3$ and titanates of the general formula $\text{Ti}(\text{OR})_4$, where each of the R radicals may be the same or different and is selected independently from

- $\text{C}_1\text{-C}_{10}$ -alkyl radicals, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isohexyl, n-octyl, 2-ethylhexyl, n-nonyl and n-decyl,

- $\text{C}_3\text{-C}_{12}$ -cycloalkyl radicals, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, and cyclododecyl; preference is given to cyclopentyl, cyclohexyl and cycloheptyl.

Each of the R radicals in $\text{Al}(\text{OR})_3$ or $\text{Ti}(\text{OR})_4$ is preferably the same and selected from isopropyl or 2-ethylhexyl.

- Examples of preferred acidic organometallic catalysts are selected from dialkyltin oxides R_2SnO where R is as defined above. A particularly preferred representative compound of acidic organometallic catalysts is di-n-butyltin oxide, which is commercially

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available as "oxo-tin", or di-n-butyltin dilaurate.

Preferred acidic organic catalysts are acidic organic compounds having, for example, phosphate groups, sulfonic acid groups, sulfate groups or phosphonic acid groups.

- 5 Particular preference is given to sulfonic acids, for example para-toluenesulfonic acid. The acidic organic catalysts used can also be acidic ion exchangers, for example sulfonic acid group-containing polystyrene resins which are crosslinked with about 2 mol% of divinylbenzene.
- 10 It is also possible to use combinations of two or more of the abovementioned catalysts. It is also possible to use an immobilized form of those organic or organometallic, or else inorganic catalysts which take the form of discrete molecules.

- If the intention is to use acidic inorganic, organometallic or organic catalysts, the amount used in accordance with the invention is from 0.1 to 10% by weight, preferably from 0.2 to 2% by weight, of catalyst.

- The inventive process is carried out under an inert gas atmosphere, i.e., for example, under carbon dioxide, nitrogen or a noble gas, among which particular mention should be made of argon.
- 20

- The inventive process is carried out at temperatures of from 60 to 200°C. Preference is given to working at temperatures of from 130 to 180°C, in particular up to 150°C or lower. Particular preference is given to maximum temperatures up to 145°C, very particular preference to temperatures up to 135°C.
- 25

- The pressure conditions for the inventive process are not critical per se. It is possible to work at distinctly reduced pressure, for example at from 10 to 500 mbar. The inventive process may also be carried out at pressures above 500 mbar. For reasons of simplicity, preference is given to the reaction at atmospheric pressure; however, it is also possible to work at slightly increased pressure, for example up to 1200 mbar. It is also possible to work at distinctly elevated pressure, for example at pressures up to 10 bar. Preference is given to the reaction at atmospheric pressure.
- 30

- The reaction time for the inventive process is typically from 10 minutes to 25 hours, preferably from 30 minutes to 10 hours and more preferably from one to 8 hours.
- 35

- Once the reaction has ended, the highly functional hyperbranched polyesters can easily be isolated, for example by filtering off the catalyst and concentrating, the concentration typically being effected at reduced pressure. Further very suitable workup methods are precipitation after addition of water, followed by washing and drying.
- 40

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Component B2) can also be prepared in the presence of enzymes or decomposition products of enzymes (according to DE-A 101 63163). In the context of the present invention, the dicarboxylic acids reacted in accordance with the invention are not included in the acidic organic catalysts.

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Preference is given to using lipases or esterases. Very suitable lipases and esterases are *Candida cylindracea*, *Candida lipolytica*, *Candida rugosa*, *Candida antarctica*, *Candida utilis*, *Chromobacterium viscosum*, *Geotrichum viscosum*, *Geotrichum candidum*, *Mucor javanicus*, *Mucor mihei*, pig pancreas, *Pseudomonas* spp., *Pseudomonas fluorescens*, *Pseudomonas cepacia*, *Rhizopus arrhizus*, *Rhizopus delemar*, *Rhizopus niveus*, *Rhizopus oryzae*, *Aspergillus niger*, *Penicillium roquefortii*, *Penicillium camembertii*, or esterase from *Bacillus* spp. and *Bacillus thermoglucosidasius*. Particular preference is given to *Candida antarctica* lipase B. The enzymes listed are commercially available, for example from Novozymes Biotech Inc., Denmark.

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The enzyme is preferably used in immobilized form, for example on silica gel or Lewatit®. The processes for immobilizing enzymes are known per se, for example from Kurt Faber, "Biotransformations in organic chemistry", 3rd edition 1997, Springer Verlag, Chapter 3.2 "Immobilization" pp. 345-356. Immobilized enzymes are commercially available, for example from Novozymes Biotech Inc., Denmark.

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The amount of immobilized enzyme used is from 0.1 to 20% by weight, in particular from 10 to 15% by weight, based on the mass of all of the starting materials used and to be reacted.

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The inventive process is carried out at temperatures above 60°C. Preference is given to working at temperatures of 100°C or lower. Preference is given to temperatures up to 80°C, very particular preference is given to temperatures of from 62 to 75°C, and even greater preference is given to temperatures of from 65 to 75°C.

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The inventive process is carried out in the presence of a solvent. Examples of suitable solvents are hydrocarbons such as paraffins or aromatics. Particularly suitable paraffins are n-heptane and cyclohexane. Particularly suitable aromatics are toluene, ortho-xylene, meta-xylene, para-xylene, xylene in the form of an isomer mixture, ethylbenzene, chlorobenzene and ortho- and meta-dichlorobenzene. Further very particularly suitable solvents are: ethers, for example dioxane or tetrahydrofuran, and ketones, for example methyl ethyl ketone and methyl isobutyl ketone.

35

The amount of solvent added is at least 5 parts by weight, based on the mass of the starting materials used and to be reacted, preferably at least 50 parts by weight and more preferably at least 100 parts by weight. Amounts of more than 10 000 parts by weight of solvent are undesirable, because the reaction rate declines markedly at

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markedly lower concentrations, which leads to uneconomically long reaction times.

The inventive process is carried out at pressures above 500 mbar. Preference is given to the reaction at atmospheric pressure or slightly elevated pressure, for example up to 1200 mbar. It is also possible to work under distinctly elevated pressure, for example at pressures up to 10 bar. Preference is given to the reaction at atmospheric pressure.

The reaction time of the inventive process is typically from 4 hours to 6 days, preferably from 5 hours to 5 days and more preferably from 8 hours to 4 days.

Once the reaction has ended, the highly functional hyperbranched polyesters can be isolated, e.g. by filtering off the enzyme and concentrating the mixture, the concentration typically being carried out at reduced pressure. Other very suitable workup methods are precipitation after addition of water, followed by washing and drying.

The highly functional hyperbranched polyesters obtainable by the inventive process feature particularly low contents of discolored and resinsified material.

For the definition of hyperbranched polymers, see also: P.J. Flory, J. Am. Chem. Soc. 1952, 74, 2718, and A. Sunder et al., Chem. Eur. J. 2000, 6, no. 1, 1-8. However, in the context of the present invention, "highly functional hyperbranched" means that the degree of branching, i.e. the average number of dendritic linkages plus the average number of end groups per molecule, is from 10 to 99.9%, preferably from 20 to 99%, more preferably from 30 to 90% (on this subject, see H. Frey et al. Acta Polym. 1997, 48, 30).

The inventive polyesters have a molecular weight M_w of from 500 to 50 000 g/mol, preferably from 1000 to 20 000 g/mol, more preferably from 1000 to 19 000 g/mol. The polydispersity is from 1.2 to 50, preferably from 1.4 to 40, more preferably from 1.5 to 30 and most preferably from 1.5 to 10. They are typically very soluble, i.e. clear solutions can be prepared using up to 50% by weight, in some cases even up to 80% by weight, of the inventive polyesters in tetrahydrofuran (THF), n-butyl acetate, ethanol, and numerous other solvents, with no gel particles detectable by the naked eye.

The inventive highly functional hyperbranched polyesters are carboxyl-terminated, carboxyl- and hydroxyl-terminated, and preferably hydroxyl-terminated.

When they are used in a mixture, the ratios of the components B1):B2) are preferably from 1:20 to 20:1, in particular from 1:15 to 15:1, and very particularly from 1:5 to 5:1.

As component C), the inventive molding compositions may comprise from 0 to 60% by weight, in particular up to 50% by weight, of other additives and processing assistants.

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For example, they may comprise stabilizers, lubricants, fillers, pigments, flame retardants, light stabilizers, blowing agents, plasticizers, polymeric processing assistants, impact modifiers, optical brighteners, antistats or biostabilizers.

- 5 Some suitable additives are described in detail below. However, the examples adduced do not constitute any restriction of the inventive mixtures, but serve merely for illustration. All data on the content are percentages by weight.

- 10 Stabilizers neutralize the hydrochloric acid released during and/or after the processing of the PVC.

Useful stabilizers are all customary PVC stabilizers in solid and liquid form, for example customary Ca/Zn, Ba/Zn, Pb or Sn stabilizers, and also acid-binding sheet silicates such as hydrotalcite.

- 15 The inventive molding compositions may have a content of stabilizers of from 0.05 to 7%, preferably from 0.1 to 5%, more preferably from 0.2 to 4% and in particular from 0.5 to 3%.

- 20 Lubricants are intended to be effective between the PVC particles and counteract frictional forces in the course of mixing, plasticizing and reshaping.

- The lubricants comprised by the inventive molding compositions may be all lubricants customary for the processing of plastics. Useful examples are hydrocarbons such as
25 oils, paraffins and PE waxes, fatty alcohols having from 6 to 20 carbon atoms, ketones, carboxylic acids such as fatty acids and montanic acid, oxidized PE wax, metal salts of carboxylic acids, carboxamides and carboxylic esters, for example with the alcohols ethanol, fatty alcohols, glycerol, ethanediol, pentaerythritol and long-chain carboxylic acids as the acid component.

- 30 The inventive molding compositions may have a content of lubricants of from 0.01 to 10%, preferably from 0.05 to 5%, more preferably from 0.1 to 3% and in particular from 0.2 to 2%.

- 35 Fillers influence in particular the compressive strength, tensile strength and flexural strength, and also the hardness and heat distortion stability, of plasticized PVC in a positive way.

- In the context of the invention, the molding compositions may also be fillers, for
40 example carbon black and other inorganic fillers such as natural calcium carbonates, for example chalk, limestone and marble, synthetic calcium carbonates, dolomite, silicates, silica, sand, diatomaceous earth, aluminum silicates such as kaolin, mica and

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feldspar. The fillers used are preferably calcium carbonates, chalk, dolomite, kaolin, silicates, talc or carbon black.

- 5 The inventive molding compositions may have a content of fillers of from 0 to 60%, preferably from 0.1 to 60%, more preferably from 0.5 to 50% and in particular from 1 to 40%.

- 10 The inventive molding compositions may also comprise pigments in order to adjust the resulting product to different possible uses.

- 15 In the context of the present invention, either inorganic pigments or organic pigments may be used. The inorganic pigments used may, for example, be cadmium pigments such as CdS, cobalt pigments such as $\text{CoO}/\text{Al}_2\text{O}_3$, and chromium pigments, for example Cr_2O_3 . Useful organic pigments are, for example, monoazo pigments, condensed azo pigments, azomethine pigments, anthraquinone pigments, quinacridones, phthalocyanine pigments, dioxazine pigments and aniline pigments.

- 20 The inventive molding compositions may have a content of pigments of from 0.01 to 10%, preferably from 0.05 to 5%, more preferably from 0.1 to 3% and in particular from 0.5 to 2%.

- In order to reduce the flammability and the evolution of smoke in the event of burning, the inventive mixtures may also comprise flame retardants.

- 25 The flame retardants used may, for example, be antimony trioxide, phosphate esters, chloroparaffin, aluminum hydroxide, boron compounds, molybdenum trioxide, ferrocene, calcium carbonate or magnesium carbonate.

- 30 The inventive molding compositions may have a content of flame retardants of from 0.01 to 10%, preferably from 0.1 to 8%, more preferably from 0.2 to 5% and in particular from 0.5 to 3%.

- 35 In order to protect articles produced from the inventive molding compositions from damage in the surface region by the influence of light, the mixtures may also comprise light stabilizers.

- In the context of the present invention, it is possible to use, for example, hydroxybenzophenones or hydroxyphenylbenzotriazoles.

- 40 The inventive molding compositions may have a content of light stabilizers of from 0.01 to 7%, preferably from 0.1 to 5%, more preferably from 0.2 to 4% and in particular from 0.5 to 3%.

In the context of the invention, the inventive molding compositions may also comprise further polymers selected from the group consisting of homo- and copolymers based on ethylene, propylene, butadiene, vinyl acetate, glycidyl acrylate, glycidyl methacrylate, acrylates and methacrylates with alcohol components of branched or unbranched C1 to C10 alcohols, styrene or acrylonitrile.

Examples include polyacrylates with the same or different alcohol radicals from the group of the C4 to C8 alcohols, particularly of butanol, hexanol, octanol and 2-ethylhexanol, polymethyl methacrylate, methyl methacrylate-butyl acrylate copolymers, methyl methacrylate-butyl methacrylate copolymers, ethylene-vinyl acetate copolymers, chlorinated polyethylene, nitrile rubber, acrylonitrile-butadiene-styrene copolymers, ethylene-propylene copolymers, ethylene-propylene-diene copolymers, styrene-acrylonitrile copolymers, acrylonitrile-butadiene rubber, styrene-butadiene elastomers and methyl methacrylate-styrene-butadiene copolymers.

The inventive thermoplastic molding compositions may be prepared by methods known per se, by mixing the starting components in conventional mixing apparatus, such as screw extruders, Brabender mixers or Banbury mixers, and then extruding them. After the extrusion, the extrudate may be cooled and comminuted. It is also possible to pre-mix individual components and then to add the remaining starting materials individually and/or likewise in a mixture. The mixing temperatures are generally from 230 to 290°C.

The inventive thermoplastic molding compositions feature good flowability with simultaneously good mechanical properties.

In particular, the processing of the individual components (without clumping or caking) is problem-free and possible in short cycle times, so that thin-wall components in particular are possible applications, with very little mold deposit.

These materials are suitable for the production of fibers, films and moldings of any type, in particular for applications in casings of electrical appliances, for example kitchen appliances and computer casings, pipelines, apparatus, cables, wire sheathing, window profiles, in interior fittings, in vehicle and furniture construction, in floorcoverings, medical items, food packaging, gaskets, films, composite films, phonographic disks, synthetic leather, toys, packaging containers, adhesive tape films, clothing, coatings, as fibers for fabrics.

Examples

Component A:

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Polyvinyl chloride having a K value to ISO 1628-2 of 57, prepared by suspension polymerization

Preparation method for polycarbonates B1

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General method:

As shown in table 1, equimolar amounts of the polyhydric alcohol and diethyl carbonate were mixed in a three-neck flask equipped with stirrer, reflux condenser, and internal thermometer, and 250 ppm of potassium carbonate (based on the amount of alcohol) were added. The mixture was then heated to 100°C with stirring and stirred at this temperature for 2 h. As the reaction progressed, the temperature of the reaction mixture was reduced as a result of the onset of evaporative cooling of the monoalcohol released. The reflux condenser was now replaced by an inclined condenser, ethanol was distilled off, and the temperature of the reaction mixture was increased slowly to 160°C.

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The ethanol distilled off was collected in a cooled round-bottom flask and weighed, and the conversion was thus determined as a percentage based on the full conversion theoretically possible (see table 1).

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The reaction products were then analyzed by gel permeation chromatography, the eluent being dimethylacetamide and the standard being polymethyl methacrylate (PMMA).

Table 1:

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	Alcohol	Catalyst	Amount of ethanol distillate based on full conversion [mol%]	Molecular weight M_w M_n	Visc 23°C [mPas]	OH number [mg KOH/g]
30	TMP · 1.2 PO	K ₂ CO ₃	90	2136 1446	7200	461

TMP ≙ Trimethylolpropane

PO ≙ Propylene oxide

35

Component C/1

Mixture of monoocetylthioesters with dioctylthioesters (Bärostab® 710N from Bärlocher)

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Component C/2

26

Epoxidized soya oil (from Cognis: Edenol® D81)

Epoxide content: 7%

Component C/3

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Pentaerythrityl tetrastearate (from Cognis: Loxiol® VPG 861)

Preparation of the molding compositions

- 10 Components A) to C) were blended at 160°C in a single-screw extruder and extruded into a water bath. After granulation and drying, test specimens were injection-molded and tested.

- 15 The granule was injection-molded into dumbbell specimens to ISO 527-2 and a tensile test was carried out. In addition, impact resistance was determined to ISO 179-2, MVR (ISO 1133) and the flow performance were tested, K value and the VN to DIN 53726 in cyclohexanone.

- 20 The inventive compositions and the results of the measurements can be taken from table 2.

Table 2:

Components [% by wt.]	1C	2	3	4
Component A	97.85	96.85	96.35	95.35
Component B	-	1.00	1.50	2.50
Component C/1	1	1.00	1.00	1.00
Component C/2	0.75	0.75	0.75	0.75
Component C/3	0.4	0.40	0.40	0.40

VN:	85.4	87.1	86.4	85.9
K value	55.4	55.9	55.7	55.6
MVR (185°C; + 21.6 kg)	2.1	4.4	2.8	5.5
Flow spirals	7.1	8.3	9.2	9.9

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Mechanical properties

Stress at max.	(N/mm)	61.8	64.7	66.8	68.2
Tensile stress at break	(N/mm)	35.3	35.5	35.6	38.9
Tensile strain at yield	(%)	3.6	3.4	3.4	3.4
Tensile strain at break	(%)	15	13.6	10.4	9.3
Modulus of elasticity: ISO 527-2	(N/mm)	3217	3268	3313	3321
Impact resistance ISO 179-2	(kJ/m ²)	319	320	314	302
Impact resistance -30°C		71	68	75	74
Notched impact resistance		1.7	1.7	1.7	1.6

C = for comparison

What is claimed is:

1. A thermoplastic molding composition comprising
 - 5 A) from 10 to 99.99% by weight of at least one polyvinyl chloride (PVC),
 - B) from 0.01 to 50% by weight of
 - B1) at least one highly branched or hyperbranched polycarbonate
or
 - 10 B2) at least one highly branched or hyperbranched polyester of the A_xB_y type
where x is at least 1.1 and y is at least 2.1
or mixtures thereof
 - C) from 0 to 60% by weight of further additives,
- 15 the sum of the percentages by weight of components A) to C) adding up to 100%.
2. The thermoplastic molding composition according to claim 1, in which component B1) has a number-average molecular weight M_n of from 100 to 15 000 g/mol.
- 20 3. The thermoplastic molding composition according to claims 1 or 2, in which component B1) has a glass transition temperature of from -80°C to 140°C .
4. The thermoplastic molding composition according to claims 1 to 3, in which component B1) has a viscosity (mPas) at 23°C (to DIN 53010) of from 50 to
- 25 200 000.
5. The thermoplastic molding composition according to claims 1 to 4, in which B 1) has an OH number of from 1 to 600 mg KOH/g of polycarbonate (to DIN 53240, part 2).
- 30 6. The thermoplastic molding composition according to claims 1 to 4, in which component B2) has a number-average molecular weight M_n of from 300 to 30 000 g/mol.
- 35 7. The thermoplastic molding composition according to claims 1 to 5, in which component B2) has a glass transition temperature T_g of from -50°C to 140°C .
8. The thermoplastic molding composition according to claims 1 to 6, in which component B2) has an OH number (to DIN 53240) of from 0 to 600 mg KOH/g of
- 40 polyester.
9. The thermoplastic molding composition according to claims 1 to 7, in which

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component B2) has a COOH number (to DIN 53240) of from 0 to 600 mg KOH/g of polyester.

10. The thermoplastic molding composition according to claims 1 to 8, in which
5 component B2) has at least one OH number or COOH number greater than 0.
11. The thermoplastic molding composition according to claims 1 to 9, in which the ratio of components B1):B2) is from 1:20 to 20:1.
- 10 12. The use of the thermoplastic molding compositions according to claims 1 to 10 for producing fibers, films and moldings of any type.
13. A fiber, film or molding of any type, obtainable from the thermoplastic molding compositions according to claims 1 to 10.

Flowable PVC

Abstract

- 5 Thermoplastic molding compositions comprising
- A) from 10 to 99.99% by weight of at least one polyvinyl chloride (PVC),
 - B) from 0.01 to 50% by weight of
 - 10 B1) at least one highly branched or hyperbranched polycarbonate
or
 - B2) at least one highly branched or hyperbranched polyester of the A_xB_y type
where x is at least 1.1 and y is at least 2.1
or mixtures thereof
 - 15 C) from 0 to 60% by weight of further additives,
- the sum of the percentages by weight of components A) to C) adding up to 100%.